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High-Pressure Methane Storage in Porous Materials: Are Carbon Materials in the Pole Position?

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ABSTRACT: Natural gas storage on porous materials (ANG) is a promising alternative to conventional on-board compressed (CNG) or liquefied natural gas (LNG). Until date, MOF materials have apparently been the only system published in the literature able to reach the new DOE value of 263 cm^3 (STP: 273.15K, 1 atm)/cm^3; however, this value was obtained by using the ideal single-crystal density to calculate the volumetric capacity. Here we prove experimentally and for the first time that properly designed activated carbon materials can really achieve the new DOE value but avoiding the additional drawback usually associated with MOF materials, i.e. the low mechanical stability under pressure (conforming) required for any practical application.

INTRODUCTION

Vehicular natural gas (VNG) has been used on a large scale for several decades.[1] Cost-efficiency and effectiveness of this alternative fuel has been already proved in vehicles (buses and cars) in many countries all around the world, e.g. Argentina. The praises of natural gas, comprising chiefly methane, compared to gasoline are the high H/C ratio that supposes higher energy per mass of fuel, a higher combustion efficiency, a lower cost and, last but not least, a much cleaner burning (it contains less carbon per unit of energy of any fossil fuel with 40% less greenhouse emissions). Nowadays developed and developing countries are considering this technology for a massive scale use to alleviate the unavoidable depletion of petroleum resources and to mitigate the large CO_2 emissions associated with actual global warming.

Despite these advantages, the main drawback of natural gas is its low energy density compared to gasoline (37 MJ/l) and diesel (32 MJ/l). One potential solution to improve the energy density is to store natural gas at high pressure (above 20 MPa) and room temperature (compressed natural gas actually used for mobile applications), with an energy density of 9.2 MJ/l or as a liquid (liquefied natural gas for long distances gas transportation) at 112 K and atmospheric pressure, with an energy density of 22.2 MJ/l. A less demanding solution in terms of pressure and temperature concerns methane storage in the nanocavities of porous materials (also called adsorbed natural gas-ANG). Adsorbed natural gas constitutes a safer and cheaper way to store methane at an acceptable gas density while working at substantially lower pressures (3.5-6.5 MPa), allowing for conformable gas deposits.

Recently, the Department of Energy of the United States (DOE) has stablished a new volumetric objective for adsorbed natural gas from the old DOE value of 180 cm^3 (STP: 273.15K, 1 atm)/cm^3 to the much ambitious value of 263 cm^3 (STP: 273.15K, 1 atm)/cm^3; the equivalent gravimetric value for the later would be 0.5 g/g.[2] This value is equivalent to the amount of compressed natural gas at 25 MPa and 298 K (ρ_{CH_4} = 11.73 mol/l). At this point it is important to highlight that the unit cm^3 (STP) is defined as the volume occupied by an ideal gas at a standard temperature and pressure. Here, STP is defined as 273.15 K and 1 atm, according to the American standards, resulting in a volume of 22.414 ml for 1 mmol of ideal gas at STP (STP conditions by the IUPAC are different, i.e. 273.15 K and 1 bar). Among the different porous materials with potential interest for high-density methane storage via physisorption, metal-organic frameworks have been proposed as the best candidates to fulfil these ambitious requirements.[3,4] In a recent paper, Peng et al. demonstrated that HKUST-1 and Ni-MOF-74 materials are able to reach the new DOE value with a total volumetric capacity of 267 cm^3/cm^3 and 251 cm^3/cm^3, respectively, at 6.5 MPa, although associated with a low gravimetric capacity (0.216 g/g and 0.148 g/g). Similar values (0.230 g/g at 100 bar and 298K) were reported for a mesoporous MOF with defined, modular pore system and a large pore volume of 2.02 cm^3/g.[5] The gravimetric value is low because authors have used the crystal density of the material – in some cases above 2.0 g/cm^3 – to calculate the apparently high volumetric capacity. Despite the potential of MOFs for high-pressure methane storage, these materials are characterized, except for some specific cases, by a low mechanical stability under pressure.[3] These limitations have under-

scored the need to move towards materials that are efficiently packable, yet capable of withstanding mechanical compression while retaining full adsorption capacity (within the new DOE values).

Nanoporous carbons (mainly activated carbons and carbon nanotubes) are an alternative material with potential interest for methane storage at high pressure.[6-8] Grand Canonical Monte Carlo Simulations have predicted idealized bundles of SWNTs and wormlike carbon pores as promising nanomaterials for effective storage of methane at moderate pressures (1-7 MPa and 293K).[7] However, experimental studies from Yang et al. using single-walled carbon nanohorn assemblies have shown that the maximum gravimetric adsorption capacity at 6 MPa and 303 K cannot exceed 0.11 g/g.[8] Recently, higher methane uptakes were reported for ordered-mesoporous carbide-derived-carbons (OM-CDC) with an excess adsorbed amount of 0.208 g/g at around 10 MPa and 298 K.[9]

Unlike MOF materials, carbon materials exhibit a higher mechanical strength avoiding any packing-related efficiency loss provided that they can be optimized in terms of gravimetric and volumetric capacity. With this in mind, this work provides an overview of the best carbon nanomaterials actually available for methane storage, both commercial carbons and novel high-surface area carbon molecular sieves developed in our research group. Excess, absolute and total (storage) amount adsorbed will be carefully revised to avoid the widespread misunderstanding frequently observed in the literature. Gravimetric and volumetric values will be evaluated at the typical pipeline pressure of 3.5 MPa, at the more relevant on-board storage pressure of 6.5 MPa (easily achievable with a cheap two-stage compressor and still allowing for conformable deposits) and up to 20 MPa. All these values together with the working capacity (deliverable capacity) will be compared for the best carbon materials and the most promising MOF described in the literature up to date, HKUST-1. Advantages and disadvantages associated with these porous systems in terms of adsorption capacity and mechanical stability will be thoroughly investigated.

EXPERIMENTAL SECTION

Three commercial activated carbons, granular F400 (Filtrasorb 400, Calgon carbon Co.), granular RGC30 (NucharRGC30, Westvaco) and Maxsorb in pellet form (The Kansai Coke and Chemicals co.); and three powder activated carbons synthesized in our laboratory, LMA405, LMA738 and LMA726, have been evaluated.

Sample LMA405: Olive stones were used as starting material. The raw material was carbonized at 773K in a horizontal furnace under inert atmosphere and a heating rate of 5K/min. The resulting material was physically mixed with KOH in a 5:1 ratio (KOH:precursor) and ground in a ball mill at 300 rpm for 30 min. Activation process was carried out in a horizontal furnace at 1073K for 2h with a heating rate of 5K/min. The synthesized material was washed, first with a 10% HCl solution and afterwards with distilled water in a Soxhlet apparatus, until complete removal of chloride ions, and finally dried overnight at 383K.

Samples LMA738 and LMA726: Two activated carbons have been prepared by chemical activation with anhydrous KOH of two mesophase pitches (PY56, for LMA738, and VR93, for sample LMA726), using KOH: precursor ratio of 8:1 and 6:1 (wt./wt.), respectively. The mesophase pitch and the KOH were initially mixed in a ball mill during 30 min, and subsequently the mixture was submitted to an activation treatment in a horizontal furnace at 1073K for 2 h, under a nitrogen flow of 100 ml/min, and using a heating rate of 5K/min. The final material was washed, first with a 10% HCl solution and afterwards with distilled water in a Soxhlet apparatus, until complete removal of chloride ions, and finally dried overnight at 383K.[10,11]

Sample HKUST-1: HKUST-1 was synthesized using the receipt described by Schlichte et al.[12] In a typical synthesis, Cu(NO3)2.H2O (0.875g, 3.6 mmol) was dissolved in 12 ml of de-ionized water (solution 1) and trimesic acid (0.42g, 2.0 mmol) in 12ml of ethanol (solution 2). The solutions 1 and 2 were mixed under stirring for 30 min, and then placed in an autoclave under hydrothermal condition, 383K for 18h.

Characterization: Textural properties of the different samples were evaluated by nitrogen adsorption measurements at 77 K using a homemade fully-automated manometric equipment designed and constructed by the Advanced Materials Group (LMA), now commercialized as N2Gsorb-G (Gas to Materials Technologies (www.g2mtech.com). The samples were previously degassed for 4 h at 523 K. Nitrogen adsorption data were used to determine: i) the total pore volume ($V_{N2,total}$) at a relative pressure of 0.95, ii) the BET specific surface area (SBET), iii) the micropore volume ($V_{N2,DR}$) by application of the Dubinin-Radushkevich equation (DR)[13] and iv) pore size distribution by applying the Quenched solid density functional theory (QSDFT; slit-shape model) to the N_2 adsorption data. The difference between $V_{N2,total}$ and $V_{N2,DR}$ is considered to be the mesopore volume (V_{meso}).

Packing density has been determined by pressing a given mass of activated carbon into a wafer with a cross-sectional area of 1.32 cm^2 at a pressure of 1 Ton, i.e. 753 kg/cm^2. Helium density, which represents the skeleton density of the carbon (ρ_{He}), was measured in a Helium pycnometer AccuPyc 1330. Samples were dried in the oven overnight before any measurement.

Methane excess adsorption capacity of the synthesized and commercial activated carbons was measured at 298 K and up to a final pressure of 10-20 MPa. Before any adsorption measurement, activated carbons were outgassed at 523 K for 4 h. These measurements were carried out in a homemade fully-automated high pressure manometric equipment (designed and constructed by the Advanced

Materials Group (LMA), now commercialized as iSorbHP by Quantachrome Corporation). This equipment takes into account the compressibility factor (Z) calculated by the Helmholtz equation[14] and the non-linear behavior caused by the differences in temperature between the manifold and the cells.

RESULTS AND DISCUSSION

The success of the adsorbed natural gas technology mainly depends on the porous characteristics of the adsorbent material that will fill the tank. Table 1 reports the textural characteristics for the six activated carbons evaluated and the metal-organic framework HKUST-1 (N2 adsorption isotherms for the different samples are shown in Figure S1). Selected activated carbons are mainly microporous (commercial F-400 and Maxsorb) or micro/mesoporous systems (commercial RGC30, petroleum pitch derived carbon molecular sieves LMA738 and LMA726 and a lignocellulosic-based LMA405 carbon). While commercial activated carbons exhibit a moderate development of porosity (S_{BET} ranges from 1000 to 1800 m^2/g), activated carbons prepared from petroleum pitch or olive stones using KOH as activating agent are characterized by an extremely large BET surface area (well in excess of 3000 m^2/g), and a highly-developed micro/mesoporous structure. Textural analysis of sample HKUST-1 provides a pore volume of 0.70 cc/g, which is consistent with previous values reported in the literature.[3,15] Taking into account that an adsorbent for supercritical CH_4 storage should have predominant microporosity, high surface area and low mesoporosity,[6] results from Table 1 anticipate that petroleum-pitch derived carbons could be excellent candidates to achieve a high storage capacity at moderate pressures.

To validate this assumption, Figure 1 shows the excess adsorption/desorption isotherms for methane at 298 K and up to 10 MPa in (a) gravimetric and (b) volumetric basis. For samples with a purely microporous network excess adsorption isotherms exhibit a maximum at moderate pressures (6-8 MPa), the excess amount adsorbed slightly decreasing thereafter. This maximum in the excess adsorption isotherm indicates an increase in the methane density in the bulk phase while the adsorbed phase density remains mainly invariable, characteristic for adsorption of supercritical fluids.[16] However, the scenario changes completely for samples combining both micro and narrow mesopores. For these samples there is a continuous increase with pressure with no maximum or decline observed. Gibbs excess uptake in gravimetric basis (g/g) at 10 MPa is in the range from 0.21 g/g to 0.26 g/g for the petroleum-pitch and olive stones derived activated carbons. Interestingly, irrespective of the final pressure these activated carbons overpass KHUST-1 material in gravimetric basis (g/g), the adsorption process being fully reversible over the whole pressure applied. To our knowledge this is the highest value published for carbon materials.

Despite the excellent adsorption behavior of activated carbons in terms of gravimetric capacity, these materials suffer from a low density compared to some MOF materials (e.g., HKUST-1). As observed in Figure 1b, the low packing density of activated carbon materials (around 0.4-0.6 g/cm^3) results in a lower volumetric capacity despite the excellent textural properties (extraordinarily high surface area and pore volume). Samples LMA738 and LMA726 with the largest development of porosity achieve a final target of 188 cm^3/cm^3 and 172 cm^3/cm^3, respectively, at 298 K and 10 MPa, well below the value achieved by HKUST-1 (258 cm^3/cm^3) and the new DOE value (263 cm^3/cm^3). At this point it is important to highlight that the excess volumetric uptakes have been calculated from the real packing density for carbon materials, while the ideal crystallographic density has been used for HKUST-1, this value being far from being realistic (a single crystal of MOF fitting the tank seems unrealistic, thus overpredicting the real volumetric adsorption capacity of the MOF). In the case of the carbon materials, a certain correlation between the methane uptake and the micropore volume ($V_{N_2,\ DR}$) is observed, in close agreement with literature.[17]

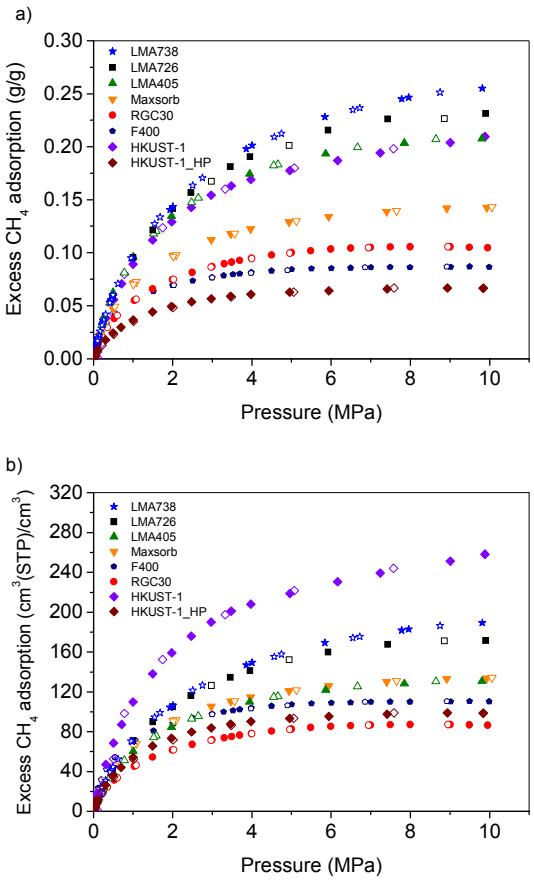

Figure 1. Excess (a) gravimetric and (b) volumetric CH_4 uptake for different activated carbon materials at 298 K. HKUST-1 material is included for the sake of comparison (closed symbols: adsorption, open symbols: desorption).

Results described in Figure 1 correspond to the Gibbs excess uptake for CH_4 in a gravimetric (g/g) or volumetric basis (cm^3/cm^3), considering the density (packing or crystallographic density) of the different samples. However,

researcher should never forget that the DOE value refers to storage uptake, that is, the total amount of gas available in a tank full with adsorbent. While the *excess* isotherms can be obtained directly from the experimental equipment, the *absolute* isotherms and the *storage* isotherms have to be estimated from the former one by applying the corresponding equations. A detailed description of the different concepts and equations can be found in the Supporting Information. Briefly, the *absolute* isotherm represents the amount of molecules in the adsorbed phase. The *absolute* uptake, sometimes erroneously called *total* uptake, is based on the knowledge of the density or the volume of the adsorbed phase through the following equation

$$\boldsymbol{n_{ads} = n_{exc} + \rho_{gas} \cdot V_{ads}} \quad (1)$$

where $\boldsymbol{n_{ads}}$ is the number of molecules in the adsorbed phase, $\boldsymbol{n_{exc}}$ is the number of molecules measured experimentally, $\boldsymbol{\rho_{gas}}$ is the density of the non-adsorbed gas and $\boldsymbol{V_{ads}}$ is the volume of the adsorbate in the adsorbed phase. Although it is generally stablished for MOFs that the adsorbed volume corresponds to the pore volume obtained from the nitrogen adsorption measurements at 77 K,[3] this is not fully correct for many porous materials (e.g., porous solids containing a pore size distribution owing to the strong dependence of the *absolute* amount adsorbed on the choice of the boundary),[18] with the corresponding error in the *absolute* isotherm.

As described above, the DOE value refers to *storage* capacity, i.e., the *absolute* amount adsorbed plus the gas in the largest pores (not estimated by nitrogen) and the gas in the interparticular space, where the gas remains with a lower density. To avoid uncertainty in the estimation of these parameters, we recommend an easy and fast way to calculate directly the *storage* isotherm from the excess isotherm using the following equation

$$\boldsymbol{n''_{stg} = n''_{exc} + \rho_{gas} \cdot \left(1 - \frac{\rho_{pack}}{\rho_{He}}\right)} \quad (2)$$

where n''_{stg} is the volumetric storage capacity and it is defined as the amount of adsorptive/adsorbate inside a tank per adsorbent volume unit, when the tank is filled with an adsorbent, and $\boldsymbol{n''_{exc}}$ is the excess adsorbed amount of the sample per adsorbent unit volume. Equation 2 allows calculating the *storage* capacity in an easy way without any approximation avoiding the unknown V_{ads}. It simply includes the skeleton density, i.e. the helium density, and the packing density, both parameters being easily measurable. Readers are referred to the Supporting Information for a detailed explanation of equation 2 together with its application to a case study (sample RGC-30; see Figure S2) and its validity by measuring the weight of a container filled with this activated carbon and pressurized with methane. Coming back to equation 2, it includes the skeleton density that is inherent to the adsorbent and the packing density or apparent density that depends on how particles are packed in the tank. In the case of carbon, the former one depends on the carbon precursor as well as the activation degree achieved. The maximum value that can achieve He density is the graphite density, i.e. 2.26 g/cm^3. It is worth mentioning that some materials can adsorb helium and consequently, the skeleton density can be overestimated. Fortunately, ± 0.1 g/cm^3 precision is acceptable when measuring He density (*ca.* 5.5% variation), since it alters the storage capacity by 1%. Concerning the packing density, it is important to highlight that this is a critical factor in the efficiency of the material since it determines the extent of volume where the gas is not adsorbed. High packing density implies that more adsorbent can fill the tank with minimal interparticle space; increasing the packing density in 0.1 g/cm^3 results in a *ca.* 6.5% improvement in the amount of methane stored.

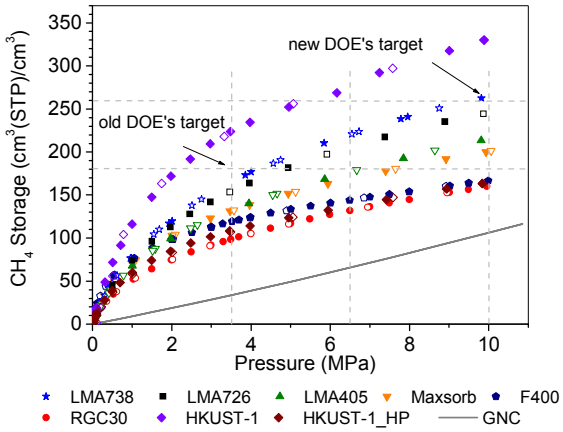

Figure 2. Methane *storage* capacity for different activated carbons at 298 K and up to 10 MPa. MOF sample HKUST-1 has been included for the sake of comparison (closed symbols: adsorption, open symbols: desorption).

The *storage* capacity for all activated carbons and the MOF sample (HKUST-1) has been estimated from the excess adsorption isotherms using equation 2. Figure 2 compares the *storage* uptake (cm^3/cm^3) for the different activated carbon samples and for the most promising MOF (HKUST-1) with the old and the new DOE targets. In close agreement with recent studies described in the literature by Hupp's group,[3] sample HKUST-1 is able to reach both the old DOE value at 3.5 MPa, with a *storage* capacity of 225 cm^3/cm^3, and the new DOE value at 6.5 MPa, with a *storage* capacity of 276 cm^3/cm^3. Concerning the activated carbon materials, the situation changes drastically depending on the textural properties of the sample. While purely microporous samples (F-400) or samples with a moderate BET surface area (RGC-30) are not able to reach the old DOE value even at 10 MPa, samples combining micro and mesopores in a perfectly defined way can do it. In fact, petroleum pitch-derived carbon molecular sieves (LMA738 and LMA726) can reach 180 cm^3/cm^3, at 4 MPa and 5 MPa, respectively. Last but not least, both samples can reach the new DOE value (263

cm^3/cm^3) although at a slightly larger pressure than sample HKUST-1, i.e. 10 MPa.

Theoretical calculations have predicted that packing density for methane in slit-shaped pores (usually present in activated carbons) can reach a maximum value when the distance between opposite walls is around 2-3 times the size of the methane molecule, i.e. 0.8-1.2 nm.[19] However, pore sizes in the mesoporous range not only assure fast adsorption kinetics but also can have a critical contribution in methane adsorption at high pressures.[20] As it can be observed in Figure S3, pores above 3 nm govern the sorption behavior at high pressures. Despite these premises, experimental results described in Figure 2 and summarized in Table 2 clearly show that activated carbon materials, even when properly designed in terms of porous structure, they cannot *apparently* compete with MOF materials in terms of *storage* capacity, at least in the pressure range suitable for domestic applications. Higher pressures (close to 10 MPa) using larger compressors are required to incorporate activated carbon materials into the pole position.

In addition to a high storage capacity, a proper material to be applied in a gas tank must achieve a high working capacity, that is, it must deliver the maximum amount of gas when the tank reaches a certain low pressure level before refueling, e.g., 0.5 MPa for a vehicle engine. Table 2 summarizes the working capacity for the different activated carbons in the pressure window range from 6.5 MPa down to 0.5 MPa. The corresponding value for sample HKUST-1 is included for the sake of comparison. As expected the highest working capacity corresponds to sample HKUST-1 with a total value of 200 cm^3/cm^3 in the pressure range evaluated. Interestingly, the advantage of MOFs compared to activated carbons in terms of methane uptake suffers a slight backward when comparing the working capacity, sample LMA738 having a value as high as 174 cm^3/cm^3. The excellent performance of activated carbons in terms of working capacity is associated with a low isosteric heat of adsorption for methane at low coverages compared to MOFs (isosteric heat of adsorption in MOFs at low coverages is slightly larger due to the initial interaction with the metal centers).[3,21] This effect can be clearly appreciated in Figure 2 with a steeper methane *storage* isotherm at low pressures in the case of HKUST-1.

Last but not least, one of the main parameters defining the suitability of a porous material to be used in a tank for gas storage concerns the packing density. As described before in equation 2, small deviations in the packing density can give rise to important improvement/deviations in the storage capacity. As a proof of concept, Figure S4 shows the evolution of the methane *storage* isotherm for sample LMA738 as a function of the packing density. For the powder sample, without any conforming step, the packing density is 0.07 g/cc (almost air) in accordance with a carbon skeleton with a high activation degree. Under these conditions the *storage* isotherm does not differ from the line corresponding to compressed natural gas. Consequently, a conforming step is mandatory to reduce/minimize/eliminate the interparticle space. Recent studies from Peng et al. have already addressed this issue for the HKUST-1 material.[3] Unfortunately, these analyses have shown that compacting the MOF into wafers under rising pressures (0.5 tons, 2 tons and 5 tons) becomes detrimental for the structural integrity of the material with more than 50% reduction in the total adsorption capacity associated with a partial collapse of the framework. To compare the effect of the conforming step in the adsorption performance, the different activated carbons and the HKUST-1 sample have been subjected to a conforming step at 753 Kg/cm^2 before being evaluated in the adsorption of N_2 at 77 K. As it can be observed in Figure S5, N_2 adsorption capacity at 77 K does not change for the different activated carbons evaluated after the conforming step. This mechanical stability under pressure is an inherent property of activated carbon materials and constitutes an important advantage to MOF materials. In fact, the same conforming step applied to HKUST-1 metal-organic framework, although improves the packing density above the crystallographic value (1.06 g/cm^3 vs 0.88 g/cm^3), this improvement is associated with i) a drastic decrease in the textural properties (see Figure S5), ii) a deterioration of the crystal structure (see Figure S6) and iii) a reduction in the adsorption performance (storage capacity at 10 MPa as low as 163 cm^3/cm^3, considering the new packing density after the conforming step). Readers are referred to Figures 1 and 2 to compare the *real* adsorption performance of HKUST-1 after the conforming step (denoted HKUST-1_HP), with that of activated carbon materials. At this point it is important to highlight that the adsorption performance described in Figures 1 and 2 for activated carbons is fully reproducible before and after the conforming step, i.e. there is no structural deterioration.

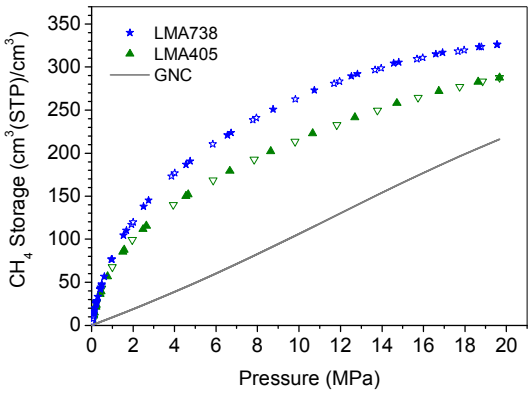

Figure 3. Methane *storage* capacity for the most promising activated carbons (LMA738 and LMA405) at 298 K and up to 20 MPa (closed symbols: adsorption, open symbols: desorption).

In summary, these results show that activated carbon materials, when properly designed, must be considered suitable materials to reach the new DOE value. Unlike MOFs, carbon materials can withstand high pressures without any damage or loss in the porosity, and conse-

quently, without any detrimental effect in the adsorption performance. These advantages make carbon materials very attractive as a component for high-pressure storage tanks both for mobile (automobile industry) or long distance transportation (gas ship-containers), provided that high-pressure compressors are available (pressures around 10 MPa are required to reach the new DOE value). Furthermore, taking into account that actual running technology in many countries is based in CNG working at 20 MPa, at these high pressures the additional incorporation of these exceptional activated carbon materials to the gas tank could be a tremendous advantage in terms of storage capacity (see Figure 3) with a 50% improvement in the amount stored (storage capacity at 20 MPa for sample LMA738 as high as 328 cm^3/cm^3) compared to conventional compressed natural gas (CNG).

ASSOCIATED CONTENT

Characterization results, additional adsorption measurements and full description of the experimental equations are included as a Supporting Information.

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Author Contributions

M.E.C. prepared the samples and performed the characterization and the adsorption test. E.G.R. developed the different equations. M.M.E., J.S.A., K.K. and F.R.R. directed the work and participated in the discussion of the results. J.S.A. and M.E.C. wrote the paper.

Notes

The authors declare no competing financial interests.

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Table 1. Textural parameters obtained from the nitrogen adsorption measurements at -196ºC. Packing density and He density are also included.

sample	S_{BET} m^2/g	$V_{N2,DR}$ cm^3/g	$V_{N2,total}$ cm^3/g	V_{meso} cm^3/g	ρ_{pack} * g/cm^3	P_{He} g/cm^3
F400	1070	0.40	0.55	0.15	0.91	2.18
RGC30	1440	0.52	1.13	0.61	0.59	1.90
Maxsorb(2040)	1800	0.64	0.83	0.19	0.67	2.22
LMA405	3551	1.00	2.00	1.00	0.45	2.20
LMA738	3290	1.10	2.25	1.15	0.53	1.80
LMA726	3425	1.11	2.44	1.31	0.54	1.90
HKUST-1	1680	0.66	0.70	0.04	0.88**	2.80**
HKUST-1_HP	930	0.36	0.39	0.03	1.06	2.80**

* ρ_{pack}, packing density or apparent density calculated by pressing the powder to 753 kg/cm^2; ** ρ_{He}, Helium density or skeleton density; *** HKUST-1 ideal single-crystal MOF and skeleton density obtained from ref. 3.

Table 2. Methane uptake for the different samples evaluated at 298 K and different pressures (3.5 MPa and 10 MPa). The working capacity is defined as the difference in methane uptake between 6.5 MPa and 0.5 MPa.

sample	Excess (3.5MPa)		Absolute (3.5MPa)		Storage (3.5MPa)		Storage (10MPa)	Working Capacity
	g/g	cm^3/cm^3	g/g	cm^3/cm^3	g/g	cm^3/cm^3	cm^3/cm^3	cm^3/cm^3
F400	0.079	100	0.084	107	0.093	119	166	90
RGC30	0.093	77	0.098	81	0.121	100	161	97
Maxsorb(2040)	0.118	111	0.125	117	0.142	133	201	123
LMA405	0.168	106	0.179	113	0.213	134	215	135
LMA738	0.191	142	0.202	150	0.222	165	265	174
LMA726	0.184	137	0.187	138	0.210	156	246	160
HKUST-1	0.164	201	0.173	212	0.182	224	330	200
HKUST-1_HP	0.059	87	0.063	91	0.073	107	163	98

SYNOPSIS TOC

High-pressure methane storage and working capacity at 298K on a wide variety of activated carbons and KHUST-1 MOF